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Selective high yield prepn. of carboxylic acid anhydride(s) - by reacting carboxylic acid ester(s) or ether(s) with carbon mon:oxide, using metal complex of nitrogen contg. polar cpd. as catalyst

C87-087734

Carboxylic acid anhydrides (I) are prepd. by reacting a carboxylic acid ester (II) or ether (III) with carbon monoxide using a metal complex catalyst (IV) co-ordinated with polar cpds. (V) contg. two or more N and fixed to banded cpd.

USE/ADVANTAGE

(I) (e.g. acetic anhydride, propionic anhydride), including mixed anhydrides (e.g. acetic propionic anhydride, acetic butyric anhydride), can be prepared in high yield and selectivity. Catalytic activity is kept high for a long time, giving (I) in reliably high yield and selectivity.

CATALYST

Suitable metals in catalyst (IV) are rhodium, iridium, ruthenium, palladium, nickel or cobalt. The polar cpds. (V) used are imidazoles, triazoles, bipyridyls, aminopyridines, pyrimidines, pyrazines, imidazopyridines, naphthylidines, pyridazines, triazines, triethylenediamines, piperazines or polymethylenediamines.

(IV) is fixed to banded cpd. by ion-exchange with ion existing between layers.

Fixed (IV) may be prepared by fixation of metal complex (having ligand except (V)) to banded compound by ion-exchange, subsequent replacement of ligand with (V).

Banded compound contg. sodium ion between layers and a part of the sodium ion is substituted with lithium, potassium, magnesium, calcium, zinc, copper, zirconium, titanium, hafnium, silicon, tin, aluminium, yttrium, scandium, lanthanum, technetium, rhenium, iron, chromium, bismuth, niobium, tantalum or vanadium may be used to fix (IV).

STARTING MATERIAL

(II) and (III) are suitably of formulae (IIa) and (IIIa)

$$R^1CO_2R^2 \quad (IIa) \qquad R^3OR^4 \quad (IIIa)$$

R^1 = 1-8C alkyl;
R^2 = 1-8C alkyl;
R^3 = 1-8C alkyl; and
R^4 = 1-3C alkyl.

PREFERRED CONDITIONS

Reaction of (II) or (III) with carbon monoxide is carried out at 100-300 °C under 10-15 kg/sq.cmG. Molar ratio of (II) or (III)/carbon monoxide is 0.1-10, esp. 0.5-4.

Accelerator, such as bromine, iodine, methyl-(ethyl - or hydrogen-)bromide(or iodide), may be used in the reaction; molar ratio of accelerator/(II) or (III) is 0.025-1.

EXAMPLE

Catalyst was prepared by supporting nickel-imidazole complex on montmorillonite. Catalyst (5g) was packed into the pipe reactor. A mixt. of methyl acetate (0.14 mol/hr), carbon monoxide (0.14 mol/hr) and methyliodide (0.014 mol/hr) was fed to reactor. Reaction was carried out at 250°C under 60 kg/sq.cmG. Conversion of methyl acetate was 12.0% and selectivity to acetic anhydride was 75.9%. (7ppW129LDDwgNo 0/0)

E(10-A25) N(2)

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